

Camphoroxalic Acid Derivatives.

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF
THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY
WITH THE REQUIREMENTS FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY.

BY

WILLIAM EDWIN HOFFMAN, JR.

1905

EASTON, PA. :
ESCHENBACH PRINTING COMPANY.

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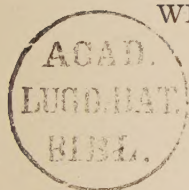
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The author gladly avails himself of this opportunity to express his gratitude to President Ira Remsen and Professors H. N. Morse, H. C. Jones, and E. B. Mathews for the valued instruction which he has received in lecture room and laboratory.

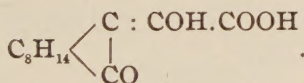
This investigation was undertaken at the suggestion of Dr. J. Bishop Tingle, and to him the writer desires to express his thanks for his coöperation and council during its pursuit. To Dr. C. E. Waters, formerly of the Johns Hopkins University, and to Dr. H. W. Doughty, of the Carnegie Institution, the author is indebted for valuable suggestions.

Camphoroxalic Acid Derivatives.

HISTORICAL.

In 1889 J. Bishop Tingle, in the course of an investigation of the action of ethereal oxalates on aliphatic ketones, found that the impure sodium camphor, obtained by the action of sodium on camphor, in boiling toluene solution, condenses with ethyl oxalate. At that time the question of the presence of the $\text{—CH}_2\text{—CO—}$ group in the camphor molecule was an open one and the first conclusive and direct proof of its occurrence was afforded by this work. Apart from the special interest which the subject thus acquired, it possessed other more general ones ; hence, the investigation of the above condensation-product, termed " ethylic camphoroxalate," was continued.

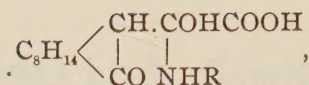
In 1897, to obtain light, if possible, on the question of the time constitution of diketones, of which camphoroxalic acid is an example. A further object was to accumulate data which might lead to a better understanding of the mechanism of the Claisen condensation. The results as regards the constitution of camphoroxalic acid are fairly complete and indicate that it is an unsaturated keto alcohol :



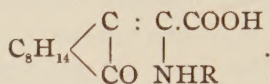
In the course of the work, a new class of compounds was discovered, formed by the condensation of the acid with amines.¹

The condensation compounds of the sodium and potassium salts of camphoroxalic acid and of the ethylester with amines, both aliphatic and aromatic, were studied. The primary products, in all cases, were, apparently, additive substances of the general type,

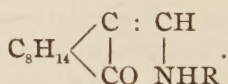
¹ J. Am. Chem. Soc., **23**, 363 (1901).



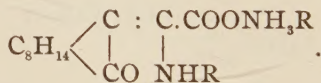
but only one compound with this formula could be isolated. It was obtained from hydroxylamine and sodium camphoroxalate, the other substances appeared to be unstable and eliminated the elements of water, giving rise to products of the general formula :



Compounds of this nature were prepared from ammonia, hydroxylamine, semicarbazine, aniline and α - and β -naphthylamine. Such substances as those formulated above might be expected to undergo further change ; carbonic anhydride might be evolved with the formation of a compound of the type :



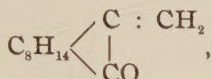
In addition to the above, a third compound of the amine with camphoroxalic acid might be formed, namely, a salt of the acid mentioned above ; this would be represented by the formula :



Representatives of these various types were actually prepared from aniline and sodium camphoroxalate. The first by the action of the constituents in a neutral solvent, at the ordinary temperature ; the second by the action of aniline and camphoroxalic acid, under pressure, at 130° , or by heating the first compound above its melting-point. The third derivative was obtained by the action of aniline on free camphoroxalic acid, in a neutral solvent, at the ordinary temperature.

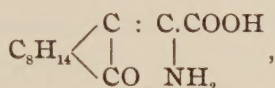
In naming these compounds the simplest and most advisable

method appeared to be to regard them as derived from the complex,

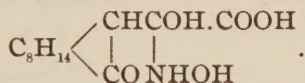


for which the term camphoformene was suggested; it is self-explanatory and indicates the presence of the double linkage.

By the action of ammonia on sodium or potassium camphoroxalate, sodium or potassium camphoformeneaminecarboxylate was obtained, from which the free acid,

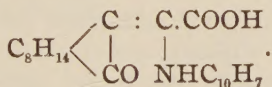


was isolated. Sodium camphoroxalate combines with hydroxylamine, forming the compound



Semicarbazine unites with potassium or sodium camphoroxalate under the same conditions as hydroxylamine. The products were thought to consist of two compounds having, apparently, the same empirical formula, but differing in their behavior toward solvents.

α -Naphthylamine reacted with sodium camphoroxalate, under somewhat similar conditions to aniline and formed α -naphthylcamphoformeneaminecarboxylic acid. The corresponding derivative of β -naphthylamine was also obtained :

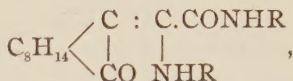


The interaction of orthophenylenediamine and sodium camphoroxalate produced camphoquinoxaline, $\text{C}_{18}\text{H}_{20}\text{N}_2\text{O}_2$.

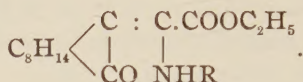
ETHYL CAMPHOROXALATE DERIVATIVES.

Methylamine, ethylamine, semicarbazine, aniline and am-

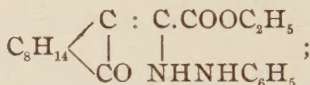
monia condensed with ethylcamphoroxalate to form compounds of the general formula,



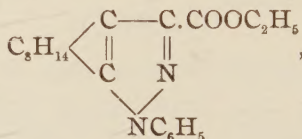
while, with aniline or β -naphthylamine, the product has the formula



Phenylhydrazine reacted with ethyl camphoroxalate forming



when this was heated above its melting-point ethyl camphyl-phenylpyrazolcarboxylate,

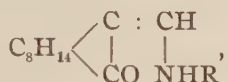


results and, on hydrolyzing this compound, the free acid was obtained.

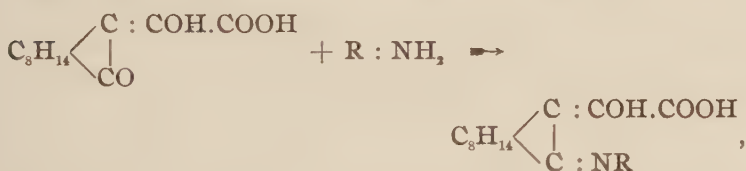
Condensation compounds could not be isolated from ethyl camphoroxalate or sodium camphoroxalate with para- and metaphenylenediamine, ethylaniline and dimethylaniline.

The object of the present investigation was to determine, if possible, what action would take place between the free camphoroxalic acid and aliphatic and aromatic amines. To ascertain, as far as possible, the limits within which the condensation takes place, to endeavor to find the cause of the inhibition of the reaction with some amines, whether it was due to stereometrical influences, to the aliphatic or aromatic nature of the amine, or to its more or less strongly developed positive properties and to try to discover the conditioning factors for

the production of substances of the varying types referred to in the preceding pages. The action of camphoroxalic acid upon a number of metallic compounds was also investigated and the typical salts of camphoroxalic acid, described below, have been prepared and analyzed. Finally, it was desired to investigate the action of acylhalides or substituted acylhalides upon compounds of the type,



the object being to endeavor to obtain evidence of the existence, in these compounds, of the group R_2NH . Although the behavior of hydroxylamine and phenylhydrazine towards ethyl camphoroxalate, which has already been referred to (pp. 5, 8) makes it highly probable that the amine attacks the group $>\text{COH}$, yet the possibility of the carbonyl group of the camphor nucleus first reacting with the amine must also be recognized; this, however, would involve the following changes:



that is, the C.OH group would remain intact and should be capable of recognition as such, but this was not found to be the case. The alternative suggestion is that intramolecular rearrangement might take place and result in the change:



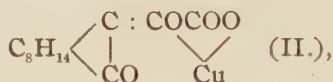
At present there is no evidence in support of this latter view, while the fact that, apart from the salt forming action of the carboxyl group, camphoroxalic acid combines with amines in equimolecular proportion would appear to be decisively against it.

METALLIC SALTS OF CAMPHOROXALIC ACID.

When cupric nitrate is allowed to react with camphoroxalic acid, in a solution of 50 per cent alcohol, at ordinary temperatures, a greenish, crystalline mass is obtained, which melts and decomposes at 275° and has the formula $C_{11}H_{14}O_4Cu$. The product is the same, irrespective of the proportions in which the copper nitrate and acid are mixed. Two views are possible of the constitution of this salt; if the copper is present in the cuprous condition, it would be



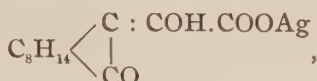
if in the cupric state, the formula



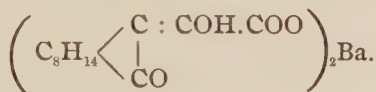
would apply and analysis could, of course, not distinguish between them. At first sight, Formula I., where the carboxyl group only is affected, would seem to be the more probable, and this view might be thought to derive support from the observation that, when the salt is heated, in alcoholic solution, at 100° , cuprous oxide is deposited. The view that the salt is represented by Formula II. is based upon the following facts: Its green color is characteristic of the cupric but not of the cuprous state. In solution the salt fails to give any indication of the presence of copper ions, which behavior is entirely in accordance with Formula II. Moreover, unlike the barium salt described below, this one gives no coloration with ferric chloride and alcohol, indicating that a change has taken place in the $:COH$ group of the camphoroxalic acid. The decomposition, on heating at 100° , is doubtless analogous to that of Fehling's solution, in which the copper is certainly in the cupric state. According to this view, the compound is a representative of a combination of two distinct types of organo-metallic derivatives, *viz.*, the salt of a carboxylic acid and the metallic deriv-

ative of a diketone, such as the sodium derivative of ethyl acetoacetate.

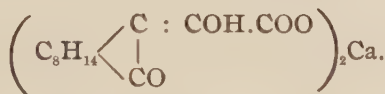
When a solution of silver nitrate, in 50 per cent alcohol, is allowed to react with camphoroxalic acid, a colorless *silver salt*,



is formed. Under similar conditions barium nitrate and camphoroxalic acid form a *barium salt*,

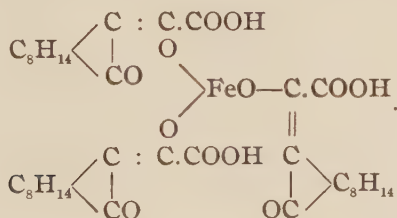


Calcium nitrate reacts in the same manner, forming the *calcium salt*,



In the case of ferric chloride and camphoroxalic acid, the compound which is formed has the characteristic, dark, reddish-violet color, which results, in general, when ferric chloride acts, in alcoholic solution, on a compound containing the enol grouping. This substance is somewhat similar to the compounds prepared by R. Schieff, in his work on acetoacetic ester when in combination with benzyl aniline.¹

Its constitution seems to be represented by the formula



¹ Ber. d. chem. Ges., 31, 205, 601.

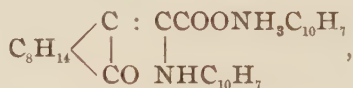
This is based on the results obtained by analysis and on the fact that the salt dissolves slowly in boiling sodium carbonate solution. It melts at about 85° .

ACTION OF AMINES ON CAMPHOROXALIC ACID.

I. β -NAPHTHYLAMINE.

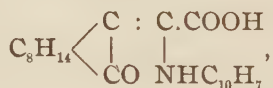
β -Naphthylamine and camphoroxalic acid yield three compounds :

1. The first of these, β -naphthylamine- β -naphthylcamphorformeneaminecarboxylate,



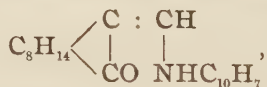
is formed in hot alcoholic solution and crystallizes in slender, pale-yellow needles, melting at 169° .

2. The second compound is obtained when this salt, in very dilute alcoholic solution, is treated with sodium hydroxide and the product acidified. β -Naphthylcamphorformeneaminecarboxylic acid,



crystallizes from alcohol in slender, bright-yellow needles, melting at $172^{\circ}.5$. This compound has been previously described by J. Bishop Tingle and Alfred Tingle.¹

3. The third compound from β -naphthylamine and camphoroxalic acid, β -naphthylcamphorformeneamine,



is formed by heating either of the preceding substances above its melting-point. It crystallizes in slender, pale-yellow prisms, melting at 173° .

¹ J. Am. Chem. Soc., **23**, 375 (1901).

II. PARATOLUIDINE.

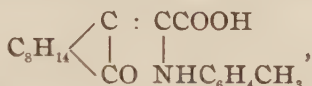
Paratoluidine and camphoroxalic acid yield a series of three compounds, corresponding to those formed by β -naphthylamine.

1. The *p*-toluidine *p*-tolylcamphoformeneaminocarboxylate,



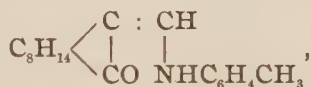
is formed in alcoholic solution and crystallizes readily from alcohol in pale-yellow needles, melting at 152° .

2. *p*-Tolylcamphoformeneaminocarboxylic acid,



is formed from the above salt by treatment with sodium hydroxide solution and subsequent acidification of the product. It crystallizes from benzene in pale-yellow prisms, melting at 168° .

3. *p*-Tolylcamphoformeneamine,



is formed by heating either of the two preceding substances above its melting-point. From alcohol it crystallizes in slender, yellow prisms, melting at 178° .

III. BENZYLAMINE.

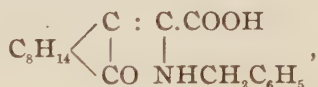
Benzylamine forms, with camphoroxalic acid, a series of three compounds, similar to those produced by β -naphthylamine and *p*-toluidine.

1. Benzylamine benzylcamphoformeneaminocarboxylate,



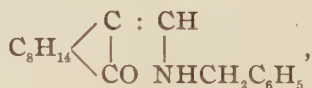
is obtained by the action of the free base on camphoroxalic acid and crystallizes from alcohol in irregular rhombohedra, melting at $174^{\circ}.5$.

2. From the above salt free *benzylcamphoformeneaminecarboxylic acid*,



is formed by treating it with sodium hydroxide and acidifying the resulting solution. It is a colorless compound, crystallizing from ethyl acetate in clusters of fine prisms, melting at 140° .

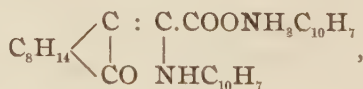
3. When heated above its melting-point, each of the preceding compounds decomposes, forming *benzylcamphoformeneamine*,



which, from alcohol, crystallizes in colorless prisms, melting at $96^{\circ}.5$.

IV. α -NAPHTHYLAMINE.

From α -naphthylamine and camphoroxalic acid two compounds are obtained; *α -naphthylamine naphthylcamphoformeneaminecarboxylate*,



is formed in alcoholic solution and, when purified by means of this solvent, yields greenish-yellow prisms, melting at 165° .

2. The above salt, when heated with sodium hydroxide solution and the product acidified, gives *α -naphthylcamphoformeneaminecarboxylic acid*,



which crystallizes from benzene with 0.5 molecule of benzene and melts at 170° .

This acid has been described by J. Bishop Tingle and Alfred Tingle.¹

3. When heated above its melting-point, each of the two preceding substances formed a viscous mass, from which no definite compound could be isolated.

V. METATOLUIDINE.

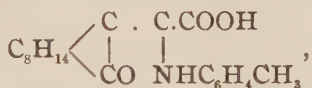
Metatoluidine and camphoroxalic acid also yield two compounds :

1. *Metatoluidine metatolylcamphoformeneaminecarboxylate*,



is formed when the free acid and amine react in alcoholic solution ; it crystallizes from alcohol in fine, pale lemon colored needles, melting at 126° .

2. The above salt, when treated with sodium hydroxide solution and the product acidified, gives *metatolylcamphoformeneaminecarboxylic acid*,

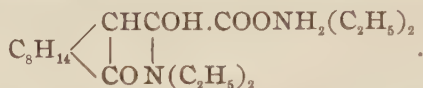


which crystallizes from benzene in colorless needles and melts at 154° . When heated above its melting-point, each of the preceding substances formed a viscous mass, from which no definite compound could be isolated.

VI. DIETHYLAMINE.

Diethylamine and camphoroxalic acid react, in alcoholic solution, to form two compounds :

¹ J. Am. Chem. Soc., **23**, 375 (1901).

1. *Diethylamine Diethylcamphoformolaminecarboxylate*,

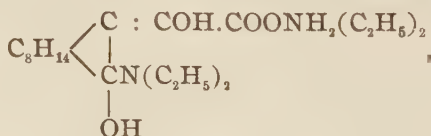
This compound crystallizes from alcohol in colorless needles, melting at $139^\circ.5$. It differs from the foregoing salts of camphoformeneaminecarboxylic acid in that its formation does not involve the elimination of the elements of water, in which respect it resembles the hydroxylamine derivative previously referred to (p. 5). With an alcoholic solution of ferric chloride no color reaction is produced. The term "*camphoformol*"

is suggested for the complex $\text{C}_8\text{H}_{14} \begin{cases} \text{CH.COHR} \\ | \quad | \\ \text{CO} \quad \text{R} \end{cases}$. It differs from "*camphoformene*" by the addition of the elements of water, one hydrogen atom being united to the camphor nucleus.

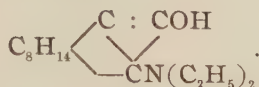
2. When this salt is heated above its melting-point it gives off water, carbonic anhydride and diethylamine and forms a compound of the same empirical formula as diethyl camphoformeneamine, $\text{C}_{15}\text{H}_{25}\text{NO}$, but which differs from what we should expect of that substance by virtue of the fact that, with ferric chloride and alcohol, it gives the reddish-violet color characteristic of the enol grouping; this seems to indicate that the reaction leading to its formation is hardly so simple as that which yields the corresponding derivatives of other amines. It may be possible that an isomeric compound,



is produced, or it may be that diethylamine and camphor-oxalic acid yield, first, the hypothetical compound,



which, when heated, would doubtless give a body with the formula

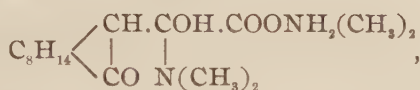


This matter will be investigated at the first suitable opportunity, because the substance in question might furnish an interesting case of dynamic isomerism.

The compound crystallizes from ethyl acetate in colorless needles, melting at 153° .

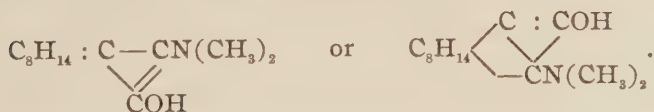
VII. DIMETHYLAMINE.

1. Dimethylamine and camphoroxalic acid, in alcoholic solution, react to form *dimethylamine dimethylcamphoformolaminecarboxylate*,



which crystallizes from acetone in colorless needles, melting at $137^\circ.5$. Like the corresponding compound from diethylamine it is, apparently, formed by the direct combination of acid and base, without the loss of a molecule of water.

2. When the salt which has just been described is heated above the melting-point, it decomposes, similarly to the analogous diethyl compound and forms a substance of the same empirical formula as dimethylcamphoformeneamine, $\text{C}_{13}\text{H}_{21}\text{NO}$, but which, on account of the fact that it gives a color reaction with ferric chloride, does not seem to have that structure. It appears probable that its constitution is similar to that of the diethyl derivative and that its formula is,



It crystallizes from alcohol in colorless needles, melting at 63° .

It is worthy of note that dimethylamine and diethylamine

are the only two secondary amines from which it has been possible to obtain derivatives with camphoroxalic acid. Methylaniline and ethylaniline entirely fail to give definite compounds under similar conditions; whether this is due to the general tendency of these two substances to yield oily salts, or to their feebler basic properties as compared with the aliphatic amines or to some other cause must, at present, remain uncertain.

VIII. METHYLAMINE.

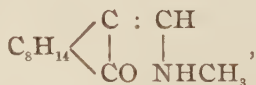
Methylamine forms two compounds with camphoroxalic acid :

1. *Methylamine methylcamphoformeneaminocarboxylate*,



which crystallizes from alcohol in slender, colorless needles, melting at 172° .

When this salt is heated above its melting-point, it forms *methylcamphoformeneamine*,



which crystallizes from ethyl acetate in colorless needles, melting at 131° .

IX. BENZAMIDINE.

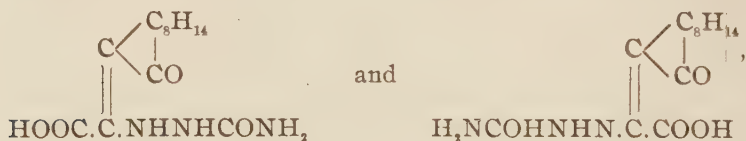
Camphoroxalic acid, in alcoholic solution, reacts with benzamidine, in equimolecular proportion, to form a colorless, crystalline compound, melting at 184° . At a slightly higher temperature it decomposes to a carbonaceous mass. Dilute acids and solutions of alkalies seem to have no effect upon the compound and ferric chloride, in alcoholic solution, does not give any color reaction. The substance has the empirical formula $\text{C}_{19}\text{H}_{24}\text{O}_4\text{N}_2$. Its constitution may, perhaps, be represented by the expression

XII. SEMICARBAZINE.

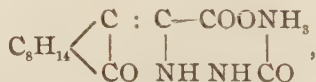
When semicarbazine and camphoroxalic acid react in the presence of acetic acid, a compound is formed with the composition of *semicarbazine camphoformeneaminecarboxylic acid*,



It crystallizes from alcohol in stout, colorless prisms, melting at 200° . When dissolved in boiling glacial acetic acid, crystals were deposited in the form of clusters of fine needles, which melt at 209° – 210° . If the compound obtained from glacial acetic acid is dissolved in sodium carbonate and reprecipitated by acid, a gelatinous substance is formed which crystallizes from acetone in slender, colorless needles, melting at the same temperature as before, *viz.*, 209° – 210° . These two substances have the same empirical formula and maintain their distinctive melting-points, even after heating for some time at 110° . They dissolve readily in sodium hydrogen carbonate and are reprecipitated by acids in the form of a jelly. With alcoholic ferric chloride, no color reaction is produced in either case. All these facts lead to one of two conclusions: either the compounds are stereoisomers of the maleic-fumaric type,



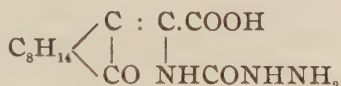
or there is the formation of an inner salt,



which is changed by the glacial acetic acid into the open-chain compound,



In the case of these semicarbazine derivatives we have represented the condensation as having taken place between the hydrazine nucleus and the camphoroxalic acid. Although this is in accordance with precedent, it may well be that in one or both compounds it is the carbamide group which has reacted, giving



and its stereoisomer. Further work will be necessary to decide between these various possibilities; the subject is being more fully investigated in this laboratory.

XIII. ORTHOPHENYLENEDIAMINE.

When orthophenylenediamine and camphoroxalic acid are allowed to react in alcoholic solution, at the ordinary temperature, there is formed the camphoquinoxaline compound, which was prepared by J. Bishop Tingle by the action of sodium camphoroxalate and also of ethyl camphoroxalate on orthophenylenediamine. It crystallizes from alcohol in bright yellow needles, which melt at 246° . The formation of this camphoquinoxaline, by the interaction of sodium camphoroxalate, ethyl camphoroxalate or camphoroxalic acid, respectively, is somewhat remarkable, as it shows the tendency of such a phenylenediamine derivative, in which the amino groups are in the ortho position, to form a five-membered ring compound, even under conditions where we should not expect such an action to take place.

PARAPHENYLENEDIAMINE was treated with camphoroxalic acid under the same conditions as were used for the ortho-compound and also under others, in the hope that it might react and throw some light on this question of ring formation, but no definite product could be obtained.

ACTION OF ACYLATING AGENTS ON CAMPHOFORMENE DERIVATIVES.

The condensation compounds from primary amines, described in the preceding pages and those previously prepared

The following table (pp. 24-25) shows the various condensation compounds of camphoroxalic acid and amines which have hitherto been prepared. They are arranged in type classes and their melting-points are given. The compounds marked * have been previously described by J. Bishop Tingle and Alfred Tingle.¹ Those marked + contain the elements of 1 molecule of water more than is shown in the type formula. Their constitution has been discussed on p. 16 *et seq.* In cases where no definite compound could be isolated, the space in the table is occupied by a dash.

EXPERIMENTAL.

Camphoroxalic acid was prepared according to the method worked out by J. Bishop Tingle² as follows :

Camphor (31.5 grams) and ethyl oxalate (22 grams) were dissolved in 400 cc. of anhydrous petroleum ether, of 85°-100° boiling-point and 3.5 grams of sodium wire were added. The mixture was boiled on a water-bath, with a reflux condenser, until the violent action had ceased and the sodium had almost entirely dissolved ; it was then allowed to remain over night, at the ordinary temperature, protected from moisture. The solution, after standing, was well shaken with about an equal volume of ice-water and the petroleum ether extract separated from the water and dried over calcium chloride. The dried liquid was distilled, at first from the water-bath; when the temperature of the boiling liquid rises to almost 90°, the pressure is somewhat reduced and the distillation continued, care being taken not to allow the temperature of the liquid in the flask to rise above 130° ; frequently it is unnecessary to heat above 120°-125°.

The aqueous solution was then well cooled and acidified with dilute sulphuric acid, then extracted three or four times with ether, until a portion of the fresh ether extract showed only a pale reddish-violet color with alcohol and ferric chloride. The ether was dried over calcium chloride and, after filtering, was distilled off and the residue added to that

¹ J. Am. Chem. Soc., **23**, 364 (1901).

² *Ibid.*, **23**, 364 (1901).

Table I.

Amines.	$\text{C}_8\text{H}_{14} \begin{array}{c} \diagup \text{C} : \text{C} \cdot \text{COONH}_3\text{R} \\ \diagdown \text{CO} \text{NHR} \end{array}$	$\text{C}_8\text{H}_{14} \begin{array}{c} \diagup \text{C} : \text{COOH} \\ \diagdown \text{CO} \text{NHR} \end{array}$ *m, p. 172°.5	$\text{C}_8\text{H}_{14} \begin{array}{c} \diagup \text{C} : \text{C} \cdot \text{CH} \\ \diagdown \text{CO} \text{NHR} \end{array}$
I. $\text{C}_{10}\text{H}_7\text{NH}_2\beta$	169°	173°	
II. $\text{C}_6\text{H}_4\cdot\text{CH}_3\cdot\text{NH}_2$ [1 : 4]	152°	178°	
III. $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{NH}_2$	147°.5	96°.5	
IV. $\text{C}_{10}\text{H}_7\text{NH}_2\alpha$	165°		
V. $\text{CH}_3\text{C}_6\text{H}_4\text{NH}_2$ [1 : 3]	126°		
VI. $\text{NH}(\text{C}_2\text{H}_5)_2$	+ 139°.5	153°	
VII. $\text{NH}(\text{CH}_3)_2$	+ 137°.5	63°	
VIII. NH_2CH_3	172°	131°	
IX. $\text{C}_6\text{H}_5\text{C}(\text{NH}_2) : \text{NH}$	—	—	
X. $\text{NH}_2\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\text{NH}_2$	—	—	
XI. $\text{CH}_3\text{C}_6\text{H}_3\text{NH}_2\text{NO}_2$	—	—	190°
XII. $\text{NH}_2\text{CONHNH}_2$	200° and 209°-210°	192°	
XIII. $\text{C}_6\text{H}_5\text{NH}_2$	*158°	*166°	
XIV. NH_2OH	—	*174°	
XV. NH_3	—	*+ 146°.5	
XVI. $\text{C}_6\text{H}_4(\text{NH}_2)_2$ [1 : 2]	—	*178°	
XVII. $\text{NH}_2\text{NHC}_6\text{H}_5$	—	—	
			$+ \text{C}_{18}\text{H}_{20}\text{N}_2\text{O}_2 \quad 246^\circ$ $+ \text{C}_8\text{H}_{14} \begin{array}{c} \diagup \text{C} : \text{C} \cdot \text{COOC}_2\text{H}_5 \\ \diagdown \text{CO} \text{NHNHC}_6\text{H}_5 \end{array} \quad 212^\circ$

Table I. (Continued).

Amines.	$\begin{array}{c} \text{C} : \text{C} \cdot \text{COONH}_3\text{R} \\ \\ \text{C}_8\text{H}_{14} \diagdown \text{CO NHR} \end{array}$	$\begin{array}{c} \text{C} : \text{C} \cdot \text{COOH} \\ \\ \text{C}_8\text{H}_{14} \diagdown \text{CO NHR} \end{array}$	$\begin{array}{c} \text{C} : \text{CH} \\ \\ \text{C}_8\text{H}_{14} \diagdown \text{CO NHR} \end{array}$
XVIII. $\text{CH}_3\text{CONHNHC}_6\text{H}_5$	_____	_____	_____
XIX. $\text{OC}(\text{NH}_2)_2$	_____	_____	_____
XX. $\text{NH}_2\text{C}_6\text{H}_4\text{NO}_2$ [1 : 4]	_____	_____	_____
XXI. $\text{CH}_3\text{COC}_6\text{H}_4\text{NH}_2$ [1 : 4]	_____	_____	_____
XXII. $\text{C}_6\text{H}_5\text{NHCH}_3$	_____	_____	_____
XXIII. $\text{C}_6\text{H}_5\text{NHC}_2\text{H}_5$	_____	_____	_____
XXIV. $\text{C}_6\text{H}_5\text{NHCH}_2\text{C}_6\text{H}_5$	_____	_____	_____
XXV. $\text{C}_2\text{H}_4(\text{NH}_2)_2$	_____	_____	_____
XXVI. $\text{C}_6\text{H}_5\text{NHNHC}_2\text{H}_5$	_____	_____	_____
XXVII. $(\text{NH}_2)_2\text{C} : \text{NH}$	_____	_____	_____
XXVIII. $\begin{array}{c} \text{CH} \diagdown \text{CH} \\ \diagup \text{CH} \diagdown \text{CH} \\ \diagup \text{N} \end{array}$	_____	_____	_____
XXIX. $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$	_____	_____	_____
XXX. $\text{CH}_3\text{C}_6\text{H}_4\text{NH}_2$ [1 : 2]	_____	_____	_____
XXXI. $\text{NH}_2\text{NHC}_6\text{H}_4\text{Br}$ [1 : 4]	_____	_____	_____
XXXII. NH_2NH_2	_____	_____	_____

from the petroleum ether extract. This residue was extracted, several times, by boiling with a 10 per cent solution of potassium hydroxide, until the filtrate, after acidification, no longer gave a marked color with alcohol and ferric chloride. The alkaline solution, from the filtered extracts, was then acidified with dilute sulphuric acid and, after standing several hours, the crystalline precipitate was filtered off. This crystalline mass was purified by recrystallization from petroleum ether, by means of a Soxhlet apparatus. The mother-liquors from the recrystallizations and the residue in the Soxhlet apparatus were treated with sodium carbonate, the solution filtered, acidified and the resulting precipitate recrystallized.

CAMPHOROXALIC ACID DERIVATIVES.

METALLIC SALTS OF CAMPHOROXALIC ACID.

Copper Camphoroxalate.—The acid (1 molecule) and copper nitrate (0.5 molecule) were separately dissolved in 50 per cent alcohol, the solutions mixed and allowed to evaporate at the ordinary temperature. Although the pure and dry copper salt does not melt below 275° , it was found that, if the solution was heated on a water-bath, to remove the excess of alcohol, the green salt formed, with part of the solvent, an oily layer which was extremely difficult to purify. When it is allowed to crystallize at the ordinary temperature, it is deposited as a fine, green, crystalline powder, which melts and decomposes at 275° . With ferric chloride, in alcoholic solution, this salt gives no coloration. If an alcoholic solution of the salt is heated for some time at 100° , it undergoes decomposition and deposits cuprous oxide. Analysis :

2.1686 grams salt gave 0.0474 gram CuO.

	Calculated for	Found.
	$\begin{array}{c} \text{C} : \text{CO} \cdot \text{COO} \\ \text{C}_5\text{H}_{14} \diagdown \quad \diagup \text{Cu} \\ \text{CO} \end{array}$	
Cu	22.28	22.46

The proportion of the reacting substances was varied, in the hope that another salt, of different composition, might be

formed, but, in all cases, the resulting compound was identical with the one described above.

2. *Silver Camphoroxalate*.—Silver nitrate and camphoroxalic acid were allowed to react in a solution of 50 per cent alcohol and, on allowing the solvent to evaporate spontaneously, a colorless, crystalline mass was obtained, which was purified by repeated recrystallization from alcohol. The resulting compound was found to melt and decompose at 137° . Analysis :

0.2975 gram salt gave 0.0965 gram Ag.

	Calculated for $\text{C}_8\text{H}_{14}\begin{matrix} \diagup \text{C} : \text{COH.COOAg} \\ \diagdown \text{CO} \end{matrix}$	Found.
Ag	32.63	32.47

As in the preparation of the copper salt, different proportions of silver nitrate and camphoroxalic acid were allowed to react but, in this case also, only one compound could be isolated.

3. *Barium Camphoroxalate*.—Barium nitrate (1 molecule) and camphoroxalic acid (2 molecules), in a solution of 50 per cent alcohol, were allowed to evaporate. These deposited a colorless, crystalline compound, which was recrystallized from alcohol. With ferric chloride and alcohol a reddish-violet color, characteristic of the presence of the enol grouping, was produced. Analysis :

0.1728 gram salt gave 0.0682 gram BaSO_4 .

	Calculated for $\left(\text{C}_8\text{H}_{14}\begin{matrix} \diagup \text{C} : \text{COH.COO} \\ \diagdown \text{CO} \end{matrix}\right)_2\text{Ba}$	Found.
Ba	23.56	23.21

The proportions of the reacting substances were varied, as in the preceding cases, but no other salt could be obtained.

4. *Calcium Camphoroxalate*.—Calcium nitrate (1 molecule) and camphoroxalic acid (2 molecules) were mixed in solution of 50 per cent alcohol, under the same conditions as in the case of the barium salt; on evaporation and recrystallization from alcohol, colorless crystals were deposited. Analysis :

0.2067 gram salt gave 0.0537 gram CaSO_4 .

	Calculated for	
	$\left(\text{C}_8\text{H}_{14} \begin{array}{l} \diagup \text{C} : \text{COH.COO} \\ \\ \text{CO} \end{array} \right)$	Found.
Ca	8.22	8.4

In the case of the calcium salt also, only one compound could be obtained.

5. *Ferric Camphoroxalate*.—Ferric chloride (1 molecule) and camphoroxalic acid (2 molecules) were mixed in solution of 50 per cent alcohol. A deep, reddish-violet coloration was produced but from no solvent could a crystalline compound be obtained and the viscous substance, deposited by the evaporation of the original liquid to dryness, gave percentages of iron which showed that it had no definite composition, hence the following method was employed: The alcoholic solution of the reaction-product, formed by the camphoroxalic acid and ferric chloride, was diluted with water in order to precipitate any unchanged camphoroxalic acid and, at the same time, to dissolve the dark-red substance in solution in the alcohol. After filtering, ether was added to the liquid, but, on account of the presence of free hydrochloric acid which had been formed by the reaction of the camphoroxalic acid and ferric chloride, the ether dissolved and formed a homogeneous solution with the original liquid. When this mixed ethereal-aqueous liquid was saturated with sodium chloride the ether took up the red compound and separated from the aqueous layer; this latter was removed and the ethereal solution dried over calcium chloride. The ether was then evaporated from the water-bath. A glassy, almost black mass remained. It is soluble, to a slight extent, in boiling sodium carbonate solution. The compound should, probably, be regarded as being camphoroxalic acid in which the hydrogen atom of the enol group :COH has been replaced by iron, while the carboxyl group remained intact on account of the presence of hydrochloric acid in the liquid during the reaction. Analysis: 0.2095 gram substance gave 0.0235 gram Fe_2O_3 .

	Calculated for	
	$\left(\text{C}_8\text{H}_{14} \begin{array}{l} \diagup \text{CCO} : \text{COOH} \\ \\ \text{CO} \end{array} \right)_3 \text{Fe.}$	Found.
Fe	7.72	7.8

AMINE DERIVATIVES OF CAMPHOROXALIC ACID.

I. β -NAPHTHYLAMINE.

1. β -Naphthylamine (6.4 grams = 2 molecules) and camphoroxalic acid (5 grams = 1 molecule) were mixed in boiling alcoholic solution, which was then kept at about 100° , on a water-bath, for a few minutes. Fine, yellow needles soon began to separate out and, on cooling, a mass of such crystals was deposited. The yield was almost quantitative. The compound is fairly readily soluble in hot alcohol and is purified by recrystallization from it. The purified compound was deposited in the form of fine needles, of a pale yellow color and melted at 169° , with the evolution of a gas. Analysis showed it to be *β -naphthylamine β -naphthylcamphoformeneaminecarboxylate*.

0.1723 gram substance gave 8.6 cc. N at 18° and 770 mm.

		Calculated for	
		C : C.COONH ₃ C ₁₀ H ₇	
		CO NHC ₁₀ H ₇	Found.
N	C ₈ H ₁₄	5.66	5.74

This salt when treated, in alcoholic solution, with ferric chloride, did not give the violet-red color characteristic of the enol grouping.

2. When the above compound is heated with a solution of sodium hydroxide, it dissolves, forming sodium β -naphthylcamphoformeneaminecarboxylate and liberating β -naphthylamine, which is deposited, on cooling the liquid and was identified by its melting-point, 112° . On acidification of the solution of the sodium salt with dilute hydrochloric acid, the free β -naphthylcamphoformeneaminecarboxylic acid is precipitated. It was purified by recrystallization from benzene and is deposited in yellow needles, melting at 172.5 – 173° . This corresponds to the melting-point obtained for the same compound which was prepared by J. Bishop Tingle.¹ The acid dissolves readily in sodium carbonate solution with the evolution of carbonic anhydride and, in alcoholic solution, produces no red color with ferric chloride.

3. When β -naphthylamine β -naphthylcamphoformeneamine-

¹ J. Am. Chem. Soc., **23**, 375 (1901).

carboxylate is heated above its melting-point, it gives off a gas which was proved to be carbonic anhydride by the production of barium carbonate, when it was led into a solution of barium hydroxide. A white solid sublimes into the upper part of the tube in which the fusion is being made and, by its melting-point, was shown to be β -naphthylamine. The fused material, after the evolution of gas had ceased, is purified by means of alcohol and crystallizes in pale yellow needles, melting at 173° . Analysis showed it to be *β -naphthylcamphoformeneamine*.

0.1783 gram substance gave 7.1 cc. N at 12° and 760 mm.

	Calculated for	
	$\text{C}_8\text{H}_{14} \begin{array}{l} \text{C} : \text{CH} \\ \\ \text{CO} \text{ NHC}_{10}\text{H}_7 \end{array}$	Found.
N	4.59	4.73

With ferric chloride, in alcoholic solution, no violet-red color was produced. When *β -naphthylcamphoformeneamine-carboxylic acid* is heated above its melting-point it gives off carbonic anhydride and forms a compound, melting at 173° , identical with that formed from the *β -naphthylamine β -naphthylcamphoformeneaminecarboxylate* by heating.

II. PARATOLUIDINE.

Camphoroxalic acid (5 grams = 1 molecule) and paratoluidine (4.8 grams = 2 molecules) were mixed in boiling alcoholic solution, which, on cooling, deposited a mass of fine yellow needles. The yield seemed to be nearly quantitative. The compound is soluble in alcohol and is purified by recrystallization from it. The purified compound crystallizes in slender, yellow needles and melts at 152° , with the evolution of a gas. With ferric chloride, in alcoholic solution, it gave no color reaction. Analysis proved it to be *paratoluidine paratolylcamphoformeneaminecarboxylate*.

0.1818 gram substance gave 10.2 cc. N at 13° and 765 mm.

	Calculated for	
	$\text{C}_8\text{H}_{14} \begin{array}{l} \text{C} : \text{C.COONHC}_6\text{H}_4\text{CH}_3 \\ \\ \text{CO} \text{ NHC}_6\text{H}_4\text{CH}_3 \end{array}$	Found.
N	6.66	6.67

2. When the above compound is heated with sodium hy-

dioxide solution, it dissolves, forming *sodium paratolylcamphoformeneaminecarboxylate* which, on acidification with dilute hydrochloric acid, precipitates the free *paratolylcamphoformeneaminecarboxylic acid*; this is insoluble in water and forms a pale yellow mass. The substance, after recrystallization from benzene, is deposited in yellow needles and melts at 168° , with the evolution of a gas. It dissolves in sodium carbonate solution with the liberation of carbonic anhydride and, with an alcoholic solution of ferric chloride, produces no color. Analysis showed it to be *paratolylcamphoformeneaminecarboxylic acid*.

0.1605 gram substance gave 6.2 cc. N at 6° and 770 mm.

	Calculated for	
	C : C.COOH	
	$\text{C}_8\text{H}_{14} \begin{array}{l} \diagup \text{C} \\ \quad \\ \text{CO} \quad \text{NHC}_6\text{H}_4\text{CH}_3 \end{array}$	Found.
N	4.47	4.64

3. When the paratoluidine paratolylcamphoformeneaminecarboxylate is heated above its melting-point it gives off a gas which was proved to be carbonic anhydride by the production of barium carbonate, when it was led into a solution of barium hydroxide. When the tube in which the fusion is being made is allowed to cool, a white, crystalline solid appears in its upper part; this, by its melting-point, $42^{\circ}.5$, was demonstrated to be paratoluidine. The fused material, after the evolution of gas had ceased, was recrystallized from alcohol and is deposited in very pale yellow crystals, melting at 178° . With alcoholic ferric chloride no color is produced. Analysis showed it to be *paratolylcamphoformeneamine*.

0.1710 gram substance gave 7.8 cc. N at 12° and 755 mm.

	Calculated for	
	$\text{C}_8\text{H}_{14} \begin{array}{l} \diagup \text{C} \\ \quad \\ \text{CO} \quad \text{NHC}_6\text{H}_4\text{CH}_3 \end{array}$	Found.
N	5.20	5.37

When paratolylcamphoformeneaminecarboxylic acid is heated above its melting-point it gives off carbonic anhydride and forms a compound, melting at 178° , identical with the one just described, which is formed by heating the paratoluidine salt of this acid.

III. BENZYLAMINE.

1. Camphoroxalic acid (5 grams = 1 molecule) and benzylamine (4.6 grams = 2 molecules) were mixed in hot alcoholic solution and, after evaporating off part of the solvent on the water-bath and cooling, a colorless, crystalline mass was gradually deposited. After recrystallization from alcohol it was obtained in the form of distorted rhombohedra, melting at $147^{\circ}.5$ with the evolution of a gas. With alcoholic ferric chloride no color was produced. Analysis showed it to be *benzylamine benzylcamphoformeneaminecarboxylate*.

0.2251 gram substance gave 15.7 cc. N at 18° and 770 mm.

	Calculated for C : C.COONH ₃ CH ₂ C ₆ H ₅ C ₈ H ₁₄ \ $\begin{matrix} \\ \text{CO} \end{matrix}$ \ $\begin{matrix} \\ \text{NHCH}_2\text{C}_6\text{H}_5 \end{matrix}$	Found.
N	7.95	8.16

2. When the above compound is heated with sodium hydroxide solution it dissolves, forming sodium benzylcamphoformeneaminecarboxylate. The addition of dilute hydrochloric acid, in excess, to this solution produces a gummy precipitate, which solidifies after standing in contact with water and, on recrystallization from ethyl acetate, forms colorless crystals, melting at 140° . In sodium carbonate solution it dissolves with the evolution of carbonic anhydride and, with alcoholic ferric chloride, produces no color. Analysis proves it to be *benzylcamphoformeneaminecarboxylic acid*.

0.2035 gram substance gave 0.5396 gram CO₂ and 0.1395 gram H₂O.

	Calculated for C : C.COOH C ₈ H ₁₄ \ $\begin{matrix} \\ \text{CO} \end{matrix}$ \ $\begin{matrix} \\ \text{NHCH}_2\text{C}_6\text{H}_5 \end{matrix}$	Found.
C	72.52	72.35
H	7.35	7.6

3. Heated above its melting-point, benzylamine benzylcamphoformeneaminecarboxylate gives off a gas which proved to be carbonic anhydride by the production of barium carbonate, when it was passed into a solution of barium hydroxide. The fused material, after the evolution of gas had

ceased, was recrystallized from ethyl acetate and is deposited in colorless prisms, melting at $96^{\circ}.5$. With alcoholic ferric chloride no color is produced. Analysis showed it to be *benzylcamphoformeneamine*.

0.1885 gram substance gave 9.8 cc. N at 16° and 762 mm.

	Calculated for	
	$\text{C}_8\text{H}_{14} \begin{cases} \text{C} : \text{CH} \\ \\ \text{CO} \text{ NHCH}_2\text{C}_6\text{H}_5 \end{cases}$	Found.
N	6.07	5.45

If *benzylcamphoformeneaminecarboxylic acid* is heated above its melting-point it also gives off carbonic anhydride and forms a compound, melting at $96^{\circ}.5$, identical with that formed by heating the *benzylamine salt* of the acid.

IV. α -NAPHTHYLAMINE.

Camphoroxalic acid (5 grams = 1 molecule) and α -naphthylamine (6.4 grams = 2 molecules) were mixed in alcoholic solution. On evaporating the solvent, greenish-yellow crystals were found which, after purification from alcohol, melt at 165° , with the evolution of gas. With ferric chloride, in alcoholic solution, no color is produced. Analysis proved it to be *α -naphthylamine α -naphthylcamphoformeneaminecarboxylate*.

0.1532 gram substance gave 7.5 cc. N at 16° and 766 mm.

	Calculated for	
	$\text{C}_8\text{H}_{14} \begin{cases} \text{C} : \text{C.COONH}_3\text{C}_{10}\text{H}_7 \\ \\ \text{CO} \text{ NHC}_{10}\text{H}_7 \end{cases}$	Found.
N	5.66	5.75

The above salt dissolves when treated with sodium hydroxide solution, forming *sodium α -naphthylcamphoformeneaminecarboxylate*, which, on acidification with dilute hydrochloric acid, forms a yellow precipitate; this, after crystallization from benzene, melts at 170° and is found to be identical with the same compound prepared in another way by Bishop Tingle. It dissolves in sodium carbonate with the evolution of carbonic anhydride and, with alcoholic ferric chloride, produces no color.

3. When either of the above α -naphthylamine compounds

was heated, in order to obtain a camphoformeneamine derivative, a gummy substance was obtained, which could not be induced to crystallize from any solvent.

V. METATOLUIDINE.

1. Camphoroxalic acid (5 grams = 1 molecule) and metatoluidine (4.8 grams = 2 molecules) were allowed to react in alcoholic solution; after evaporation there were deposited fine needles of a pale lemon color which, when recrystallized from alcohol, melted at 126°. With alcoholic ferric chloride no color was produced. Analysis showed this substance to be *metatoluidine metatolylcamphoformeneaminocarboxylate*.

0.3153 gram substance gave 19 cc. N at 25° and 765 mm.

	$\begin{array}{c} \text{C}_6\text{H}_{14} \begin{array}{l} \diagup \text{C} : \text{C} \cdot \text{COONH}_3\text{C}_6\text{H}_4\text{CH}_3 \\ \diagdown \text{CO} \quad \\ \quad \text{NHC}_6\text{H}_4\text{CH}_3 \end{array} \end{array}$	Calculated for	
N	6.66	Found.	
			6.78

2. The above salt, when treated with a solution of sodium hydroxide, dissolves, forming *sodium metatolylcamphoformeneaminocarboxylate*, which, on acidification with dilute hydrochloric acid, gives a yellow precipitate. After purification from benzene, crystals are deposited melting at 154°. They dissolve in sodium carbonate solution with the evolution of carbonic anhydride and, with alcoholic ferric chloride, give no color. Analysis shows it to be *metatolylcamphoformeneaminocarboxylic acid*.

0.1497 gram substance gave 5.65 cc. N at 10° and 770 mm.

	$\begin{array}{c} \text{C}_6\text{H}_{14} \begin{array}{l} \diagup \text{C} : \text{C} \cdot \text{COOH} \\ \diagdown \text{CO} \quad \\ \quad \text{NHC}_6\text{H}_4\text{CH}_3 \end{array} \end{array}$	Calculated for	
N	4.47	Found.	
			4.58

3. Both metatolylcamphoformeneaminocarboxylic acid and its metatoluidine salt, on heating, gave a gum, which could not be obtained pure enough for analysis.

VI. DIETHYLAMINE.

1. Camphoroxalic acid (5 grams = 1 molecule) was allowed to react with an alcoholic solution (3.4 grams = 2 molecules)

of diethylamine ; a compound crystallizing in colorless needles was obtained which, when purified by recrystallization from alcohol, melts at $139^{\circ}.5$ with the evolution of a gas. With alcoholic ferric chloride it gives no color reaction. By analysis the compound is shown to be *diethylamine diethylcamphoformolaminecarboxylate*.

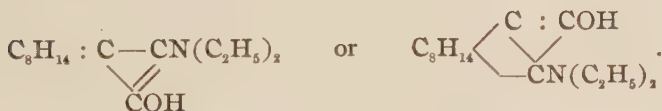
0.1983 gram substance gives 13.4 cc. N at 21° and 769 mm.

Calculated for $\text{C}_8\text{H}_{14}\left\langle \begin{array}{l} \text{CH} \cdot \text{COH} \cdot \text{COONH}_2(\text{C}_2\text{H}_5)_2 \\ \text{CO} \quad \text{N}(\text{C}_2\text{H}_5)_2 \end{array} \right.$		Found.
N	7.55	7.80

The diethylamine solution used in the preparation of this compound was prepared by dissolving diethylamine hydrochloride in absolute alcohol, adding the required amount of potassium hydroxide and filtering off the insoluble potassium chloride.

2. When treated with sodium hydroxide solution the carboxylate just described dissolves but, on acidification with dilute hydrochloric acid, it is decomposed into camphoroxalic acid and diethylamine. No method of treatment could be devised by which free diethylcamphoformolaminecarboxylic acid could be obtained.

3. When diethylamine diethylcamphoformolaminecarboxylate is heated above its melting-point, diethylamine, water and carbonic anhydride are given off and, after purification of the fused material, by crystallization from acetone, the product melts at 153° . With alcoholic ferric chloride the reddish-violet color is produced, which is so characteristic of the enol grouping. By analysis it is found to have an empirical formula identical with that of diethylcamphoformeneamine, but, on account of its behavior towards ferric chloride, its constitution seems, as previously explained (p. 16), to be represented by the formula



Analysis :

0.2045 gram substance gave 8.1 cc. N at 16° and 762 mm.

	Calculated for $C_{16}H_{25}ON$.	Found.
N	4.56	4.68

VII. DIMETHYLAMINE.

1. Camphoroxalic acid (5 grams = 1 molecule) and dimethylamine (2 grams = 2 molecules) were allowed to react in alcoholic solution and, after part of the solvent had evaporated spontaneously, a crystalline compound was obtained. After recrystallization from acetone, colorless needles were deposited, melting at 137°.5 with the evolution of a gas. With alcoholic ferric chloride it produced no color reaction. Analysis showed it to be *dimethylamine dimethylcamphoformolaminecarboxylate*. Analysis :

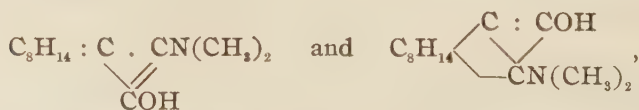
I. 0.2000 gram substance gave 0.4452 gram CO_2 and 0.1661 gram H_2O .

II. 0.2135 gram substance gave 0.4818 gram CO_2 and 0.1770 gram H_2O .

	Calculated for $C_8H_{14} \begin{matrix} \diagup CH.COH.COONH_2(CH_3)_2 \\ \diagdown CO \quad \\ \quad N(CH_3)_2 \end{matrix}$.	Found.	
		I.	II.
C	61.14	60.71	61.58
H	9.55	9.29	9.27

2. When dimethylamine dimethylcamphoformolaminecarboxylate is treated with sodium hydroxide solution it dissolves but, on acidification with dilute hydrochloric acid, decomposes into camphoroxalic acid and dimethylamine.

3. When heated to 140°, dimethylamine dimethylcamphoformolaminecarboxylate gives off water, carbonic anhydride and dimethylamine and forms a compound which, when purified by recrystallization from acetone, melts at 63°. With alcoholic ferric chloride it gives a purple color. The alternative formulæ,



for this compound are discussed on p. 16. Analysis :

0.2458 gram substance gave 14.8 cc. N at 19° and 770 mm.

	Calculated for $C_{18}H_{21}ON$.	Found.
N	6.77	7.01

VIII. METHYLAMINE.

1. Camphoroxalic acid (5 grams = 1 molecule) and methylamine (2.8 grams = 2 molecules) were mixed in alcoholic solution. After evaporation of part of the solvent, colorless needles were deposited; they were purified by recrystallization from alcohol and melted at 172°. With alcoholic ferric chloride no color reaction was produced. Analysis proved the compound to be *methylamine methylcamphoformeneaminecarboxylate*. Analysis:

0.2147 gram substance gave 20 cc. N at 14° and 766 mm.

	Calculated for C : $C_8H_{14}COONH_3CH_3$	Found.
	$ \begin{array}{c} C_8H_{14} \begin{cases} \diagup C : COONH_3CH_3 \\ \diagdown CO \end{cases} \\ \\ NHCH_3 \end{array} $	
N	10.51	11.04

2. When treated with sodium hydroxide, the above salt dissolves but, on acidification with dilute hydrochloric acid, decomposes into camphoroxalic acid and methylamine.

3. Upon heating at 175°, methylamine methylcamphoformeneaminecarboxylate gives off methylamine and carbonic anhydride and forms a compound which, when recrystallized from ethyl acetate, melts at 131°. With alcoholic ferric chloride no color reaction is produced. Analysis proved it to be *methylcamphoformeneamine*. Analysis:

0.2131 gram substance gave 13.3 cc. N at 11° and 766 mm.

	Calculated for C : $C_8H_{14}COCH_3$	Found.
	$ \begin{array}{c} C_8H_{14} \begin{cases} \diagup C : CH \\ \diagdown CO \end{cases} \\ \\ NHCH_3 \end{array} $	
N	7.25	7.50

IX. BENZAMIDINE.

Free benzamidine (2.2 grams = 1 molecule) was obtained by dissolving the hydrochloride in absolute alcohol, adding the required amount of potassium hydroxide and filtering off the insoluble potassium chloride. When camphoroxalic acid (5

grams = 1 molecule) is allowed to react with such an alcoholic solution of benzamidine and the solvent is permitted to evaporate spontaneously, a compound is obtained which may be purified by recrystallization from alcohol. It is deposited in colorless prisms; these melt at 184° , evolve a gas, char and decompose. With alcoholic ferric chloride no color reaction is produced and neither acid nor alkali seem to cause any change in the composition of the compound. When heated above its melting-point, it decomposes completely to a carbonaceous mass, from which it is impossible to obtain any definite compound. It did not dissolve in sodium carbonate solution. Analysis proved it to have the empirical formula $C_{19}H_{24}O_4N_2$. Its probable constitution is discussed on p. 19.

0.1539 gram substance gave 0.3723 gram CO_2 and 0.0963 gram H_2O .

0.2147 gram substance gave 15.5 cc. N at 19° and 766 mm.

	Calculated for $C_{19}H_{24}N_2O_4$	Found.
C	66.27	65.93
H	6.97	7.002
N	8.14	8.30

X. BENZIDINE.

Camphoroxalic acid (5 grams = 1 molecule) and benzidine (4 grams = 1 molecule) were mixed in hot alcoholic solution. When cooled, this deposited a dense mass of greenish-yellow, microscopic needles, which, on account of its very sparing solubility in all the ordinary organic media, was extracted with ether, to remove any camphoroxalic acid and benzidine. The residue, after this treatment, formed a fine powder, which gave no color reaction with alcoholic ferric chloride and was not affected by acids or alkalies. It melts at 190° and, when heated above this temperature, it decomposed to a carbonaceous mass. It is insoluble in sodium carbonate. Analysis proved it to have the empirical formula $C_{24}H_{26}O_3N_2$; its possible constitution is discussed on p. 19.

0.1489 gram substance gave 9.4 cc. N at 21° and 775 mm.

	Calculated for $C_{24}H_{26}O_3N_2$	Found.
N	7.18	7.31

XI. PARANITROORTHOTOLUIDINE.

When camphoroxalic acid (5 grams = 1 molecule) and nitrotoluidine (6.8 grams = 2 molecules) are heated at 150°, under pressure, in alcoholic solution, for 4 hours, a yellow compound is obtained which is purified by recrystallization from alcohol. It is deposited in bright yellow needles, melting at 192°. This compound is unaffected by acids or alkalies, does not dissolve in sodium carbonate and produces no color reaction with ferric chloride, in alcoholic solution. Considerable difficulty was experienced in the combustion of the substance for the determination of nitrogen; even when the heating was done most cautiously, explosions occurred, so that the analytical results were unreliable. These explosions were probably due to the presence of the nitro group in the compound. The difficulty was overcome, in a thoroughly satisfactory manner, by mixing the substance with aluminium powder; under these conditions the nitrogen was evolved during the combustion in a stream which could be easily regulated. Analysis:

0.2145 gram substance gave 8.8 cc. N at 17° and 765 mm.

Calculated for		Found.
$\text{C}_8\text{H}_{14} \begin{cases} \text{C} : \text{CH} \\ \text{CO} \end{cases} \text{NHC}_6\text{H}_3(\text{CH}_3)\text{NO}_2$		
N	4.66	4.79

XII. SEMICARBAZINE.

Semicarbazine hydrochloride (5 grams = 2 molecules) was dissolved in as little cold water as possible and added to an alcoholic solution of potassium acetate (5 grams = 2 molecules); this solution was then mixed with an alcoholic solution of camphoroxalic acid (5 grams = 1 molecule). After evaporation of most of the alcohol on the water-bath the solution was greatly diluted with water; a white, crystalline precipitate was produced which, on purification by recrystallization from alcohol, formed colorless prisms, melting at 200°. When dissolved in boiling glacial acetic acid and precipitated by the addition of alcohol, clusters of colorless, microscopic needles are deposited; these melt at 209°-210° and correspond to the

compound described by Bishop Tingle,¹ as one of two substances formed by the action of semicarbazine on potassium camphoroxalate, in alcoholic solution, at 100°, under pressure. The presence of a second compound, stated by him to be deposited from acetone in colorless needles, melting at 218°, was not observed; it is, apparently, not formed under the conditions employed by us. When the compound melting at 209°–210°, obtained from acetic acid solution, was dissolved in sodium carbonate solution and precipitated by acids it formed a jelly which, after having been dried and recrystallized from acetic acid, had the same melting-point as before, *viz.*, 209°–210°. If the original compound from alcohol, melting at 200°, is recrystallized from acetone, its melting-point remains constant. With alcoholic ferric chloride neither substance produces a color reaction. Both dissolve readily in sodium carbonate and, as has been stated, are precipitated by acids from this solution as colorless jellies. Analysis showed that both compounds have the composition of *semicarbazinecamphoformeneaminocarboxylic acid*.

0.2145 gram substance gave 0.4373 gram CO₂ and 0.1261 gram H₂O.

	Calculated for C ₈ H ₁₄ C : C.COOH CO NHNHCONH ₂	Found.
C	55.6	55.5
H	6.76	6.57

The possible constitution and relationship of these compounds has been discussed on p. 20.

XII. ORTHOPHENYLENEDIAMINE.

Camphoroxalic acid (5 grams = 1 molecule) and orthophenylenediamine (2.4 grams = 1 molecule) were allowed to react in alcoholic solution. The evaporation of the solvent yielded a deposit of fine yellow needles, which melt at 246°. This substance is identical with the compound obtained by J. Bishop Tingle.² The proportional quantities of the reacting

¹ J. Am. Chem. Soc., **23**, 373 (1901).

² *Ibid.*, **23**, 375 (1901).

materials and the conditions of the experiment were varied, but, in all cases, the same compound was obtained.

The action of camphoroxalic acid on acetylphenylhydrazine, carbamide, paranitraniline, paramineacetophenone, methylaniline, ethylaniline, benzyaniline, ethylenediamine, benzylphenylhydrazine, quinoline, pyridine, dimethylaniline, orthotoluidine, parabromphenylhydrazine and hydrazine was tried, under conditions similar to those already described for other amines, but in no case could a definite compound be obtained. The reaction-products were usually gummy substances which could not be obtained in a crystalline form. They were heated for some time at 150° – 180° , in the hope of forming compounds of the camphoformeneamine type, but from these products also no crystalline derivatives could be isolated by the use of the ordinary organic solvents.

Possibly further investigation of the compounds may result in their purification by distillation, under very low pressures.

ACTION OF ACYLATING AGENTS ON CAMPHOFORMENEAMINE DERIVATIVES.

Paratolylcamphoformeneamine (3 grams = 1 molecule) and acetyl chloride (2.6 grams = 3 molecules) were boiled in solution of anhydrous ether, for about 6 hours; the ether was then evaporated, leaving a compound which crystallized from alcohol in colorless needles, melting at 161° . Analysis showed it to be *acetyl paratolylcamphoformeneamine*.

0.1056 gram substance gave 0.2992 gram CO_2 and 0.0705 gram H_2O .

0.5403 gram substance gave 0.0983 gram $\text{Mg}_2\text{P}_2\text{O}_7$ = 0.0747 gram $\text{C}_2\text{H}_3\text{O}$.

	Calculated for	Found.
	$\begin{array}{c} \text{C}_8\text{H}_{14} \begin{array}{l} \diagup \text{C} : \text{CH} \\ \quad \\ \text{CO} \quad \text{N} \end{array} \begin{array}{l} \diagdown \text{C}_6\text{H}_4\text{CH}_3 \\ \diagdown \text{COCH}_3 \end{array} \end{array}$	
C	77.4	77.26
H	7.74	7.47
CH_3CO	13.78	13.82

Phenylcamphoformeneamine was treated with phenylsul-

phonic chloride, by the Schotten-Baumann method; (1 gram = 1 molecule) of phenylcamphoformeneamine was shaken with (1 gram = 7 molecules) of sodium hydroxide, in 10 per cent aqueous solution and (3.5 grams = 5 molecules) of phenylsulphonic chloride, which were added alternately and in small quantities; a compound is finally obtained which, by crystallization from benzene, is deposited in stout, colorless needles, melting at 133°. Analysis shows it to be *phenylcamphoformeneaminephenylsulphone*.

0.2246 gram substance gave 0.1311 gram BaSO₄.

Calculated for		Found.
$ \begin{array}{c} \text{C}_8\text{H}_{14} \begin{array}{l} \diagup \\ \text{C} : \text{CH} \\ \diagdown \end{array} \begin{array}{l} \diagup \\ \text{CO} \\ \diagdown \end{array} \text{N} \begin{array}{l} \diagup \\ \text{C}_6\text{H}_5 \\ \diagdown \end{array} \text{O}_2\text{SC}_6\text{H}_5 \end{array} $		
S	8.10	8.07

β -Naphthylcamphoformeneamine (2 grams = 1 molecule) and chloracetyl chloride (2.1 grams = 3 molecules), when boiled for some hours, in anhydrous ether, react to form a bright red substance, which was purified by distillation under diminished pressure. It boiled at 116°, under 45 mm. pressure and condensed to a colorless, crystalline solid, which could be further purified by means of petroleum ether. From this it was deposited in colorless needles, melting at 63°. The compound dissolved in sodium hydrogen carbonate, with evolution of carbonic anhydride and gave no color reaction with ferric chloride. It is very unstable and consequently could not be obtained in a state of purity sufficient to give concordant results on analysis.

BIOGRAPHICAL.

William Edwin Hoffman, Junior, was born in Baltimore, Maryland, January 27, 1881. He received his early education in the Baltimore City College and after one year in Deichmann's College Preparatory School, entered the Johns Hopkins University in October, 1899. After devoting the following three years to the completion of the Chemical-Geological course he received the degree of Bachelor of Arts in June, 1902. In October, 1902, he entered the Johns Hopkins University as a student of Chemistry. His subordinate subjects have been Physical Chemistry and Mineralogy.

